

### 515. Studies in Spectroscopy. Part IV.\* The Infra-red and Ultra-violet Spectra of Some Aliphatic Nitro-compounds.

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Infra-red spectra of the compounds  $R\cdot NO_2$  [ $R = Me, Et, Pr^n, Pr^i, Bu^n, n-C_5H_{11}, n-C_6H_{13}, MeO\cdot CH_2\cdot CH_2, CH_2EtCl, CMe_2Cl, CH_2\cdot CO_2Et, CBr_3, CCl_3, CClF_2\cdot CF_2, \text{ or } C(NO_2)_3$ ] have been recorded. The marked influence of  $R$  on the asymmetric and symmetric stretching vibrations of the  $NO_2$  group, and on the C-N stretching vibration, is discussed.

The nitro-compounds show characteristic absorption in the ultra-violet region, at *ca.* 280  $m\mu$ , and only slight shifts occur on replacement of  $\alpha$ -hydrogen by chlorine or fluorine. Bromopicrin shows no maximum in this region, and steric effects are postulated. Nitroalkanes, alkyl nitrites, and alkyl nitrates are readily distinguished by their ultra-violet spectra.

THE ultra-violet and infra-red spectra of a series of unsubstituted and halogeno-nitroalkanes have been recorded in connection with studies on fluoro-nitro-compounds described in another series (Haszeldine, *J.*, 1953, 2075).

Table 1 records the infra-red spectra of the compounds studied. The assignments made for the asymmetrical stretching (st.-a.) and symmetrical stretching (st.-s.) vibrations of the  $NO_2$  group and for the C-N stretching vibration are shown, with other bands in these regions of the spectrum. The Raman spectra of liquid nitromethane, nitroethane, 1-nitropropane, and 2-nitropropane have been recorded by Smith, Pan, and Nielsen (*J. Chem. Phys.*, 1950, **18**, 706), and the Raman spectra of a series of nitro-compounds have been reported by Wittek (*Z. physikal. Chem.*, 1942, *B*, **51**, 103, 187), and the relevant data from these papers have been included in Table 1 for comparison.

The unsubstituted nitroalkanes (and methyl 2-nitroethyl ether) of Table 1 (a) show a very characteristic st.-a. vibration near 1550  $cm^{-1}$  which changes in position only slightly with change in  $R$ . The st.-s. vibration lies in the 1430—1330- $cm^{-1}$  region which contains other bands arising from the C-H vibrations, but consideration of the infra-red and Raman spectra shows that the st.-s. band falls within the narrow range 1380—1360  $cm^{-1}$ . The C-N stretching vibration appears as a strong band in the spectra of the simpler molecules, and although it becomes more difficult to distinguish from the skeletal vibration in the more complex molecules, a definite assignment can be made.

Table 1 (b) shows the effect of an electron-attracting group (Cl or  $CO_2Et$ ) substituted on the  $\alpha$ -carbon atom. The st.-a. band moves to higher frequency, whereas the st.-s. band moves to lower frequency; there is no significant change in the C-N stretching vibration.

Table 1 (c) shows that when the nitro-group is attached to a powerful electron-attracting group, there is a further shift of the st.-a. and st.-s. vibrations to higher and lower frequency, respectively. The C-N assignments are tentative in view of multiple structure in the 920—850- $cm^{-1}$  region. The shifts to higher frequency of the st.-a. band are correlated with the increased inductive effect of the group  $R$ , an effect noted earlier with C=O stretching vibrations (Haszeldine, *Nature*, 1951, **168**, 1028).

The ultra-violet spectra of certain nitro-compounds are shown in Table 2. Earlier work on the ultra-violet spectra of nitro-compounds indicated that they gave a band near 270  $m\mu$  (Zelinsky and Rosanoff, *Z. physikal. Chem.*, 1912, **78**, 629; Kortum, *ibid.*, 1939, *B*, **43**, 271; Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 504). The present study has shown that unsubstituted nitroalkanes (and methyl 2-nitroethyl ether) are characterised by a band of low intensity near 280  $m\mu$ , whose position moves only slightly with increase in molecular weight of  $R$  in  $R\cdot NO_2$ . No difference in spectrum can be detected between primary and secondary unsubstituted nitro-compounds. The usual slight shift to the red is observed on changing the solvent from ethanol to light petroleum, and the spectra of the vapours show that solvent effects are small.

Table 2 also shows that a small but distinct bathochromic effect is obtained on replacement of an  $\alpha$ -hydrogen atom by the auxochrome chlorine; the effect of solvent is again

\* Part III, *J.*, 1953, 1764.

TABLE 1. Infra-red and Raman spectra (bands in  $\text{cm.}^{-1}$ ) of compounds  $\text{R}\cdot\text{NO}_2$ .

R		$\text{NO}_2$ st.-a.	$\text{NO}_2$ st.-s.	C-N st.	Other bands 1650—1250	Other bands 920—850
Section (a).						
Me	I.R.	1567 (vs)	1379 (s)	917 (s)	1422 (m), 1404 (s), 1311 (w)	—
	Raman	1563	1376	918	—	—
Et	I.R.	1550 (vs)	1368 (vs)	874 (s)	1460 (s), 1439 (s), 1395 (vs), 1330 (m), 1255 (m)	—
	Raman	1555	1366	875	—	—
$\text{Pr}^n$	I.R.	1553 (vs)	1385 (vs)	870 (m) or 799 (s)	1460 (s), 1437 (s), 1344 (m), 1290 (w), 1287 (w)	897 (m)
	Raman	1555	1383	872	—	—
$\text{Pr}^t$	I.R.	1553 (vs)	1361 (vs)	851 (s)	1471 (s), 1399 (vs), 1374 (m), 1304 (m)	901 (m)
	Raman	1555	1357	851	—	—
$\text{Bu}^n$	I.R.	1550 (vs)	1381 (vs)	857 (s)	1466 (s), 1435 (s), 1300 (w), 1277 (w)	912 (m)
	Raman	1558	1383	—	—	—
$n\text{-C}_5\text{H}_{11}$	I.R.	1550 (vs)	1381 (vs)	876 (s)	1464 (s), 1437 (s), 1277 (m)	—
	Raman	1550	1379	—	—	—
$\text{CHMe}_2\cdot\text{CH}_2$	I.R.	—	—	—	—	—
	Raman	1550	1389	—	—	—
$\text{CHMeEt}$	I.R.	—	—	—	—	—
	Raman	1553	1355	—	—	—
$n\text{-C}_6\text{H}_{13}$	I.R.	1550 (vs)	1381 (vs)	836 (s)	1464 (s), 1437 (s), 1276 (w)	893 (m), 870 (m)
	Raman	—	—	—	—	—
$\text{MeO}\cdot\text{CH}_2\cdot\text{CH}_2$	I.R.	1565 (vs)	1370 (vs)	876 (s) or 848 (s)	1460 (s), 1422 (s), 1395 (s)	—
	Raman	—	—	—	—	—
Section (b).						
$\text{CHEtCl}$	I.R.	1570 (vs)	1340 (s)	848 (s)	1460 (s), 1435 (s), 1374 (s), 1299 (m)	877 (m)
$\text{CMe}_2\text{Cl}$	I.R.	1565 (vs)	1340 (vs)	850 (s)	1456 (s), 1395 (s), 1376 (s)	—
$\text{CH}_2\cdot\text{CO}_2\text{Et}$	I.R.	1570 (vs)	1337 (s)	859 (s)	1471 (w), 1449 (w), 1372 (s)	—
Section (c).						
$\text{CBr}_3^*$	I.R.	1592 (vs)	1305 (vs)	838 (m)	1397 (w)	807, 796 (s. doublet)
	Raman	1592	1305	840	—	—
$\text{CCl}_3^*$	I.R.	1610 (vs)	1307 (vs)	842 (m)	1350 (m), 1277 (w)	895 (s), 858 (s)
	Raman	1605	1307	841	—	—
$\text{CClF}_2\cdot\text{CF}_2^1$	I.R.	1618 (vs)	1274 (vs)	909 (s)	1416 (w), 1350 (s)	821, 816 (s. doublet)
	Raman	—	—	—	—	—
$\text{C}(\text{NO}_2)_3$	I.R.	1618 (vs)	1266 (vs)	—	1645 (m), 1439 (w), 1370 (m)	990 (w), 973 (m)

m = medium, s = strong, vs = very strong, w = weak, s. doublet = strong doublet.

<sup>1</sup> Vapour spectrum.

\* Copies of these spectra may be obtained from the Chemical Society ( $\text{Br}_3\text{C}\cdot\text{NO}_2$ , C.S. 47;  $\text{Cl}_3\text{C}\cdot\text{NO}_2$ , C.S. 48).

small. It shows too that further introduction of chlorine on the  $\alpha$ -carbon atom causes a shift of the maximum to shorter wave-length. This cannot be attributed to chlorine acting as an auxochrome, since a further shift to the red would have been observed (see Part III, *loc. cit.*), or to the increased inductive effect of the  $\text{CCl}_3$  group relatively to the  $\text{CCl}$  group, since the fluorine compound, with the strongly electronegative  $\text{CF}_2$  group adjacent to the nitro-group, shows a maximum at  $282.5\ \mu$ , and fluorine is a less effective auxochrome than chlorine. It is suggested, therefore, that in chloropicrin there is slight steric inhibition of resonance in the nitro-group. This is supported by the complete absence of a maximum or an inflection in the absorption spectrum of bromopicrin in the  $240\text{--}450\text{-}\mu$  region. Bromine is a better auxochrome than chlorine, and if anything a shift to the red would have been expected. The spectrum of bromopicrin is, in effect, that of the  $\text{CBr}_3$  part of the molecule ( $\text{CBr}_4$  has  $\epsilon_{280}$  290). This suggests steric inhibition of resonance in the  $\text{NO}_2$  group with distortion of the  $\text{ONO}$  and/or  $\text{ONC}$  angles from their usual values. It is noteworthy that steric hindrance to coplanarity of the oxygen atoms with carbon and nitrogen in structures such as (I), with consequent reduction in intensity

of absorption, has been noted in aromatic nitro-compounds containing alkyl groups *ortho* to the nitro-group (Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838).

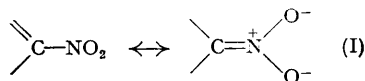
The nitroalkanes are more readily distinguished from the isomeric nitrites by their

TABLE 2. *Ultra-violet spectra (light petroleum solution).*

	$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\min.}$	$\epsilon_{\min.}$		$\lambda_{\max.}$	$\epsilon_{\max.}$	$\lambda_{\min.}$	$\epsilon_{\min.}$
MeNO <sub>2</sub> .....	278	20	245	7	CH <sub>3</sub> EtCl·NO <sub>2</sub> .....	283·5	28	249	13·5
	275 <sup>1</sup>	9	—	—		280·5 <sup>2</sup>	30	251	17
EtNO <sub>2</sub> .....	278·5	20	245·5	6	CMe <sub>2</sub> Cl·NO <sub>2</sub> .....	283·5	28	248·5	8
Pr <sup>n</sup> NO <sub>2</sub> .....	280	23	247	10		282·5 <sup>2</sup>	29	251	11
Pr <sup>i</sup> NO <sub>2</sub> .....	280	22	245·5	5·5					
Bu <sup>n</sup> NO <sub>2</sub> .....	279	22	250	12	CCl <sub>3</sub> ·NO <sub>2</sub> .....	278·5	52	247·5	16
	277 <sup>2</sup>	25	248	15		276·5 <sup>2</sup>	62	255·5	45
<i>n</i> -C <sub>6</sub> H <sub>13</sub> ·NO <sub>2</sub> .....	279	26	246	9		277 <sup>1</sup>	18	245	7
MeO·CH <sub>2</sub> ·CH <sub>2</sub> ·NO <sub>2</sub>	277·5	23	245·5	7	CClF <sub>2</sub> ·CF <sub>2</sub> ·NO <sub>2</sub>	282·5 <sup>1</sup>	48	236·5	6
<i>n</i> -C <sub>5</sub> H <sub>11</sub> O·NO .....	384	21	382	20	CB <sub>3</sub> ·NO <sub>2</sub> .....	General absorption: $\epsilon_{300}$ , 85; $\epsilon_{250}$ , 400; $\epsilon_{260}$ , 1000; $\epsilon_{240}$ , 1800.			
	370	45	364·5	31	C(NO <sub>2</sub> ) <sub>4</sub> .....	General absorption			
	356·5	56	349·5	30	BuO·NO .....	384·5	33	381·5	31
	344	50	338	24		370	70	364	49
	333	37	327	19		356	87	349	46
	323	25	318·5	17		344	77	337·5	36
	313·5	20	311	19		333	56	326·5	27
	218·5	1120	—	—		323	37	318	23
						314	27	310·5	24
						222	1700	—	—
					EtO·NO <sub>2</sub> .....	Inflection 255—260 m $\mu$ ; $\epsilon$ , 17.			

<sup>1</sup> Spectrum of vapour.  
Ethanol solution.

ultra-violet spectra than by their infra-red spectra. Butyl and amyl nitrite, for example, show strong absorption at 220 m $\mu$  and multiple weak absorption bands in the 320—380-m $\mu$  region (Table 2; cf. nitrohexane, nitrobutane). Aliphatic nitrates show only an inflection at *ca.* 260 m $\mu$  (Table 2; see also Braude, *Ann. Reports*, 1945, for references to earlier work on nitrites and nitrates).



A combination of ultra-violet and infra-red spectra can thus throw much light on to the structures of unknown nitrogen-containing compounds.

#### EXPERIMENTAL

*Compounds.*—Dr. A. I. Vogel, who kindly supplied specimens of many of the compounds shown in Table I, has reported their physical properties elsewhere. Bromo- and chloro-picrin were obtained from Messrs. Kodak. The 1-chlorotetrafluoro-2-nitroethane was prepared as described in *J.*, 1953, 2075. All specimens were redistilled immediately before use.

*Apparatus.*—The infra-red spectra were recorded on a Perkin-Elmer Model 21 instrument with rock-salt optics. The vapour spectrum was recorded, a 10-cm. gas cell with sodium chloride windows being used.

The ultra-violet spectra were determined on a Unicam Spectrophotometer, using 1- or 10-cm. silica cells. The light petroleum used as solvent had b. p. 60—80°, and was purified by treatment with fuming sulphuric acid. Ethanol (95%) was dried over calcium oxide and distilled in an atmosphere of nitrogen.

*Results.*—The infra-red spectra of the first four compounds of Table I were substantially the same as those recorded by Smith *et al.* (*loc. cit.*).

In addition to the bands recorded in Table I (c), bromopicrin showed absorption at 2899 cm.<sup>-1</sup> (very weak) and 664 cm.<sup>-1</sup>, and chloropicrin showed bands at 733 (weak), 707 (medium), and 669 cm.<sup>-1</sup> (medium).

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